

# COATINGS. ENAMELS

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## PRODUCTION OF CERAMIC PIGMENTS WITH DIOPSIDE AND ANORTHITE STRUCTURE USING THE GEL METHOD

M. B. Sedel'nikova<sup>1</sup> and V. M. Pogrebenkov<sup>1</sup>Translated from *Steklo i Keramika*, No. 8, pp. 26–28, August, 2006.

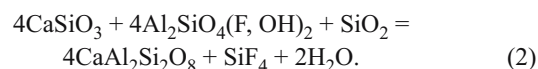
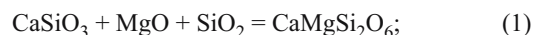
The possibility of producing ceramic pigments with the diopside and anorthite structures by the sol-gel method using wollastonite is studied. It is established that the use of the gel method intensifies the synthesis of anorthite and diopside crystal structures by means of better homogenization of the batch components at the mixing stage. A positive factor is the effective formation of anorthite and diopside structures at relatively low temperatures (about 1100°C), as well as the mineralizing effect of the chromophores on the crystallization of these minerals.

New trends are currently observed in the production of ceramic pigments. The traditional industrial synthesis from pure oxides and metal salts gives good results, since pigments produced in this way have good chromophore properties and are resistant to the aggressive effect of glazes and fluxes and to high firing temperatures. However, the drawbacks of the traditional technology include its high production cost due to expensive raw materials and high synthesis temperatures, as well as the limited number of minerals that can serve as the basis for the crystal structures of pigments.

An alternative way is producing ceramic pigments from natural minerals. The use of natural minerals makes it possible to synthesize pigments at lower temperatures, and their production cost decreases as well. However, natural crystal-line structures have a limited capacity for absorbing colorant ions; therefore, pigments based on them cannot always compete with traditional pigments in their color characteristics. New techniques are needed to produce ceramic pigments based on natural minerals, which would improve the chromophore properties of pigments [1].

Our study focuses on producing ceramic pigments with the diopside and anorthite structures by the gel method using wollastonite.

The synthesis is performed according to the following reactions:



The initial raw materials included wollastonite from the Slyudyanskoe deposit with mineral content of 95.5% (here and elsewhere wt.%, unless otherwise specified) and topaz concentrate from the Kopna deposit with topaz content of 90.3% (Table 1).

The minerals underwent fine milling to a residue not more than 2% on a No. 0063 sieve.

To synthesize pigments with the anorthite structure, we prepared a mixture of wollastonite, topaz concentrate, and silicon oxide, which stoichiometrically provides the anorthite composition (reaction (2)). The batch contained a required quantity of the specified mixture, as well as 5–20% chro-

<sup>1</sup> Tomsk Polytechnical University, Tomsk, Russia.

TABLE 1

Raw material	Weight content, %							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	calcination loss, %
Topaz concentrate	35.89	48.19	0.13	0.10	0.19	0.39	—	15.11
Wollastonite	51.70	0.11	46.48	1.23	—	0.04	0.13	0.32

TABLE 2

Pigment	Weight content, %			Weight content of chromophores, %						Color at firing temperature 1050°C
	CaSiO <sub>3</sub>	MgO	topaz	SiO <sub>2</sub>	CoO	NiO	CuO	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	
With diopside structure										
DG-3	49.68	8.57	—	25.69	16.06	—	—	—	—	Pale purple
DG-5	46.22	—	—	23.90	29.88	—	—	—	—	Dark lilac
DG-6	52.85	16.40	—	27.33	—	3.42	—	—	—	Beige
DG-11	52.73	16.36	—	27.27	—	—	3.64	—	—	Light beige
DG-16	51.05	15.85	—	26.41	—	—	—	6.69	—	Light green
DG-18	42.65	7.35	—	22.06	—	—	—	27.94	—	Greeni
DG-21	50.87	15.79	—	26.32	—	—	—	—	7.02	Sandy
DG-23	42.03	7.25	—	21.74	—	—	—	—	28.98	Red-brown
KhP	53.70	18.52	—	27.78	—	—	—	—	—	—
With anorthite structure										
AG-3	31.50	—	49.43	4.07	10.00	—	—	—	—	Sky-blue
AG-5	35.21	—	55.24	4.55	—	5.00	—	—	—	Beige
AG-6	33.36	—	52.33	4.31	—	10.00	—	—	—	Light pistachio
AG-15	31.50	—	49.43	4.07	—	—	—	15.00	—	Beige
AG-18	33.36	—	52.33	4.31	—	—	—	—	10.00	Light brown
KhP	37.06	—	58.15	3.83	—	—	—	—	—	—

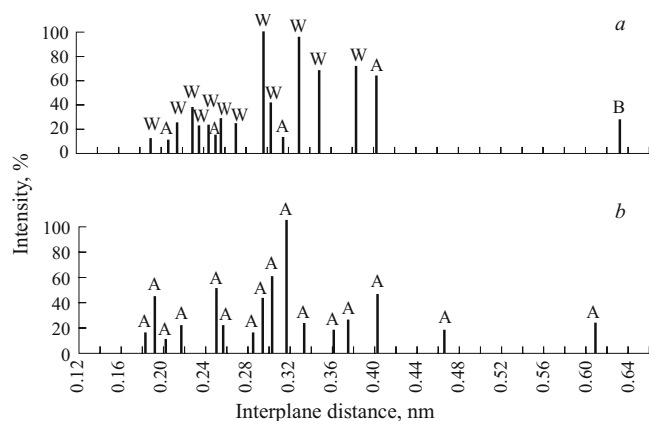
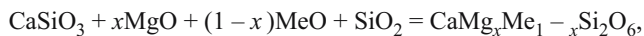


Fig. 1. X-ray diffraction patterns of the blank sample (a) and pigment AF-2 containing 10 wt.% CoO (b): W) wollastonite; A) anorthite.

mophore converted to oxide. The compositions of some pigments and their colors are listed in Table 2.

In producing pigments with the diopside structure, chromophores were introduced to replace MgO according to the following reaction



where  $x = 0, 0.1, 0.3, 0.5, 0.7$ , and  $1.0$  mole.

TABLE 3

Pigment	Paint color	Pigment	Paint color
DG-1	Blue	AG-2	Blue
DG-3	Dark blue	AG-6	Yellow-brown
DG-6	Light lettuce	AG-9	Light turquoise
DG-16	Light green	AG-15	Dark brown

The chromophores in both reactions were water-soluble salts. The pigments were produced by the following method. A small quantity of concentrated hydrochloric acid was introduced into the mixture of wollastonite with the additional oxides and chromophore salts. The resulting gel was dried and fired at 1000, 1050 and 1100°C. The resulting sinter was crushed to a residue not more than 0.2% on a No. 0063 sieve.

Some iron- and cobalt-bearing pigments at the maximum firing temperature passed into the melt. The pigments were tested as underglaze paints for painting majolica articles, which were fired at 1050°C. The colors of some underglaze paints are given in Table 3.

Analysis of the colors of pigments and paints shows that pigments with the diopside structure have a brighter tint than those with the anorthite structure.

Anorthite pigments with CoO have a sky-blue or blue shade, which points to the tetrahedral coordination of the cobalt ion, whereas diopside pigments with CoO have a lilac-purple shade caused by the coexistence of both tetrahedral and octahedral complexes. The tint of many pigments varies and becomes brighter when reacting with the glaze. Thus, diopside-based cobalt pigments under the glaze change their tint from lilac to purple-blue.

X-ray phase analysis demonstrated that the synthesis of anorthite according to reaction (2) is a multistage process. As the temperature increases to 800 – 1000°C, topaz starts transforming into mullite [2]. Although the blank sample synthesized at 1050°C partly retains its topaz structure ( $d = 0.367, 0.320$ , and  $0.296$  nm), mullite is registered as well ( $d = 0.336$  and  $0.252$  nm). Wollastonite is also registered ( $d = 0.405, 0.383$ , and  $0.280$  nm).

As the temperature grows to 1100°C, we observe small peaks typical of anorthite ( $d = 0.315, 0.252$ , and  $0.208$  nm), but the predominant structure is wollastonite (Fig. 1a).

TABLE 4

Pigment	Chromaticity coordinates		Wavelength, nm	Tone purity, %
	<i>x</i>	<i>y</i>		
AG-3	0.26	0.28	680	16
AG-6	0.42	0.38	585	47
DG-18	0.38	0.49	564	72
DG-21	0.42	0.39	582	52
DG-23	0.52	0.35	604	63

All chromophore additives in any quantity facilitate the formation of the anorthite structure in the pigments (Fig. 1b). As the weight content of NiO grows to 15% and that of Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> grows to 10%, we observe the diffraction peaks typical of these oxides, but the main structure is anorthite.

The blank sample (Fig. 2) synthesized according to reaction (1) from a mixture of wollastonite gel with magnesium and silicon oxides at a temperature of 1100°C exhibits wollastonite ( $d = 0.760, 0.404$ , and  $0.386$  nm), as well as diopside ( $d = 0.323$  and  $0.202$  nm) and okermanite ( $d = 0.352, 0.285$ , and  $0.175$  nm).

Chromophores have a different mineralizing effect on diopside formation (Figs. 2 and 3). Upon adding 0.1 mole (3.42%) CoO, single diopside peaks with low intensity appear against the background wollastonite structure. Adding 0.5 mol (16%) CoO stimulates the formation of the diopside crystalline structure, which is manifested in the increased intensity of the diffraction peaks  $d = 0.299$  and  $0.252$  nm (Fig. 2). With CoO concentration equal to 1 mole (about 30%), the diopside structure becomes the prevalent one. Additives NiO and Fe<sub>2</sub>O<sub>3</sub> have a less intense influence on diopside crystallization; the main structure here is wollastonite. Furthermore, when their concentration is equal to 0.5 mole, we observe some peaks typical of these oxides. The additives of Cr<sub>2</sub>O<sub>3</sub> generally have no effect on the formation of diopside, wollastonite persists as the main structure, and free chromium oxide is formed.

The color characteristics of the pigments were calculated based on the spectral reflection curves registered with a SF-18 spectrophotometer (Table 4).

Thus, the use of the gel method intensifies the synthesis of the crystalline anorthite and diopside structures due to a better homogenization and averaging of the batch components at the mixing stage and also due to amorphyzation of wollastonite.

It can be stated that the process of incorporation of chromophore ions in the reaction of producing the anorthite structure from topaz and wollastonite is more intense when the gel method is used, since the free form of the colorant oxides is registered when their content is 10 – 15%, whereas

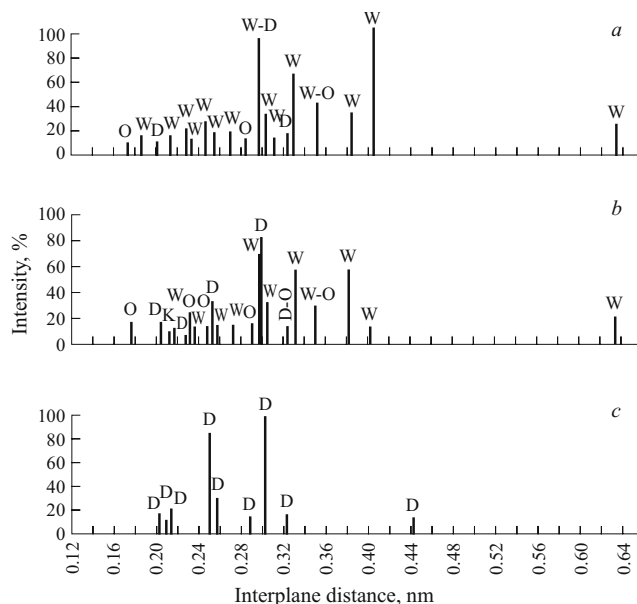


Fig. 2. X-ray diffraction patterns of the blank sample (a), pigment DG-3 containing 0.5 mol CoO (b), and pigment DG-5 containing 1.0 mole CoO (c): W) wollastonite; D) diopside, O) okermanite; K) CoO.

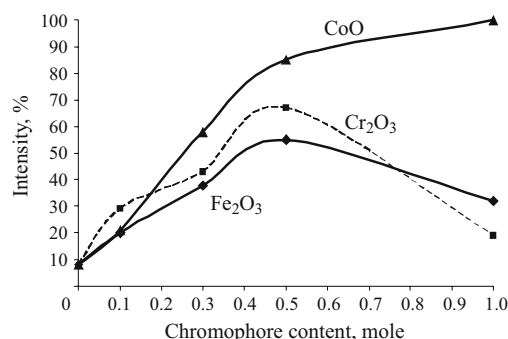


Fig. 3. Variation of the intensity of the diopside main diffraction peak ( $d = 0.299$  nm) depending on the chromophore content: wollastonite  $\rightarrow$  diopside (gel) reaction.

in the absence of the gel method free oxides are observed when their content is over 5%.

The advantages of this method include the effective formation of anorthite and diopside structures at relatively low temperatures (about 1100°C) and the mineralizing effect of the chromophores on the crystallization of these minerals.

## REFERENCES

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